PB-227 776

NATIONAL WATER QUALITY NETWORK. REPORT ON ANALYTICAL REFERENCE SAMPLE TYPE II, BD-2

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

June 1960

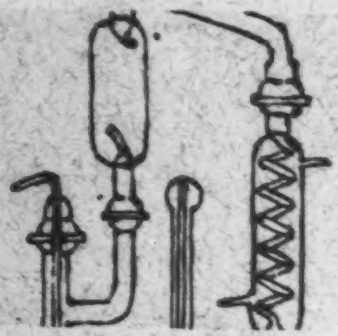
DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

050034

PB 227 776

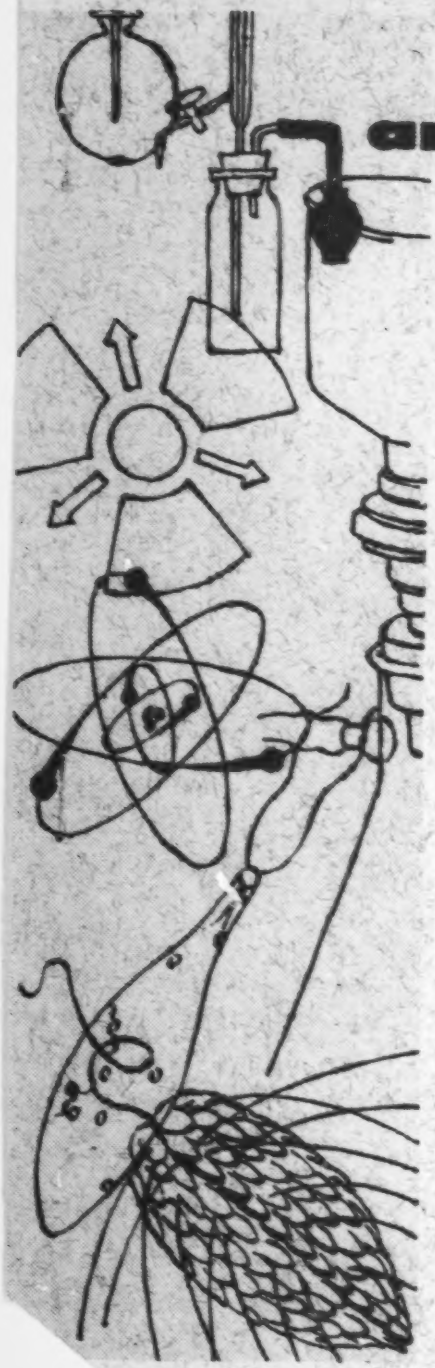


NATIONAL WATER QUALITY NETWORK

report on analytical reference sample

TYPE II, BD-2

JUNE, 1960



Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

U.S. DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
Public Health Service

ROBERT A. TAFT
SANITARY ENGINEERING CENTER

Cincinnati, Ohio

18

Participants in Study of Type II-BD 2
(Distributed January, 1960)

Louisiana State Department of Health
Regional Laboratory
Alexandria, Louisiana

Massachusetts Dept. of Public Health
Amherst, Massachusetts

Bismarck Water Department
Bismarck, North Dakota

North Dakota State Dept. of Health
Public Health Laboratory
Bismarck, North Dakota

Brownsville Water Department
Brownsville, Texas

Erie County Laboratory
Buffalo, New York

Cairo Water Company
Cairo, Illinois

Crown Zellerbach Corporation
Central Research Department
Camas, Washington

Tennessee Valley Authority
Stream Pollution Control Laboratory
Chattanooga, Tennessee

City Water Department
Cincinnati, Ohio

Board of Water Commissioners
Water Works Park Filtration Plant
Detroit, Michigan

Dubuque Water Department
Dubuque, Iowa

Duluth Water Department
Duluth, Minnesota

East St. Louis Water Company
East St. Louis, Illinois

City Water Plant
Grand Junction, Colorado

Hagerstown Water Department
Hagerstown, Maryland

Huntington Water Corporation
Huntington, West Virginia

Board of Public Utilities
Kansas City, Kansas

Massachusetts StateDept. of Health
Lawrence Experiment Station
Lawrence, Massachusetts

Arkansas Water Pollution Control Comm.
Little Rock, Arkansas

Pennsylvania Power & Light Co.
Martins Creek, Pennsylvania

City of Memphis
Light, Gas and Water Division
Memphis, Tennessee

Chemical-Toxicological Laboratory
Louisiana State Health Department
New Orleans, Louisiana

Mississippi State Board of Health
Jackson, Mississippi

Metropolitan Utilities District
Omaha, Nebraska

Philadelphia Water Department
(Belmont Laboratory)
Philadelphia, Pennsylvania

Oregon State Sanitary Authority
Portland, Oregon

International Business Machine Corp.
Poughkeepsie, New York

Participants (cont.)

City of St. Louis Water Department
St. Louis, Missouri

St. Louis County Water Co.
University City, Missouri

Minneapolis-St. Paul Sanitary Dist.
St. Paul, Minnesota

Montana-Dakota Utilities Co.
Sidney, Montana

Union Bag-Camp Paper Corporation
Savannah, Georgia

St. Joseph Water Company
St. Joseph, Missouri

Corps of Engineers
Dalecarlia Filtration Plant
Washington, D. C.

Weiser Water Department
Weiser, Idaho

Yankton Water Department
Yankton, South Dakota

INTRODUCTION

Much of the physical and chemical data reported by the Public Health Service National Water Quality Network in its annual compilation of water quality data are the result of the cooperative efforts of laboratories located at or near the sampling sites. Because these analyses originate from different sources, it is necessary that they be comparable as to accuracy. The reference sample technique is the mechanism by which this objective is being attained.

In this technique a reference solution is prepared containing known concentrations of specific elements or compounds which are then analyzed by the cooperating agencies. The results of determinations performed on the reference sample is useful in judging the quality of data submitted by the individual laboratories. Of equal importance to the cooperating agencies, is that errors in technique or method may be detected which would pass unnoticed in normal laboratory routine.

REPORT ON THE ANALYTICAL REFERENCE SAMPLES TYPE II, BD-2

This Type II reference sample is the second attempt to evaluate the procedures and techniques involved in the determination of the "demand" type analyses so important to water quality evaluation. Because it is practically impossible to provide standard samples for the direct determination of these parameters, due to changes which occur with time, the approach used was indirect. By preparing standard solutions, which when added to raw samples produce measurable and precise effects on the samples, errors in technique, procedure, or other factors which affect these tests can be discovered and thus alert the cooperating laboratories and the program to possible sources of error.

This sample was distributed as three separate solutions, Solution A, for the dissolved oxygen test. Solution B, for the B.O.D. and C.O.D. tests and Solution C for the ammonia nitrogen test.

Reasons for failure to obtain accurate results were discussed in the Type II, BD-1 report of May, 1959 and consequently are not explained as completely in this report. A table is appended, however, in which sources of errors or pitfalls for the various determinations are tabulated. In addition, staff members of the National Water Quality Network are ready to assist each cooperating agency with its specific problems whenever requested.

The standard solutions were so prepared that when a specified volume was added to a duplicate sample the difference would be a precise, measurable quantity. Deviations from the expected difference would thus serve to indicate the proficiency of the laboratory performing the measurement. From the results obtained on the previous Type II sample as well as this one, it is believed that the dissolved oxygen and ammonia determinations can be performed with good accuracy and precision. For the chemical oxygen demand and biochemical oxygen demand tests, however, the difference due to the reference sample, Solution B is not a truly precise quantity.

Specifically, Solution B is a standard solution of glucose in distilled water. The theoretical chemical oxygen demand of this solution may be accurately calculated, but the experimental result frequently does not agree with this figure, simply because the glucose is not completely oxidized by the dichromate reflux reaction. In practice about 95 percent of the glucose may be oxidized. For this study, therefore, the precision limits have been defined so that any result falling between 26.6 mg/l, the theoretical C.O.D. and 25.2, the experimental value, is accepted as a correct result and the permissible deviation of 3.2 mg/l is taken from the minimum of 25.2 and the maximum of 26.6 mg/l. The complete range for an acceptable result becomes 22.0 to 29.8 mg/l C.O.D.

For the biochemical oxygen demand test the same reasoning is also true, but the reasons for failure to attain the expected biochemical oxidation of the glucose are more variable. B.O.D. results are influenced by lack of active biological forms (seed organisms) and by lack of nutrient elements such as nitrogen and phosphorus in raw waters. This is particularly true for several laboratories in the National Water Quality Network where raw waters are known to be deficient in the ingredients necessary for optimum B.O.D. reaction rate. A correct result for the B.O.D. measurement is defined as any figure between 2.8 mg/l, the theoretical value and 2.5 mg/l, the experimental value.

The basis for this reasoning was obtained from a study on B.O.D. - C.O.D. rates, Sample Type VII, recently completed by the Analytical Reference Service of the SEC, wherein 36 agencies performed B.O.D. and C.O.D. determinations on a standard sample. The results of that study were as follows:

	B.O.D. mg/l	C.O.D. mg/l
Theoretical	220 ± 10	308
Found	198	289
% Recovered, All Groups	90%	93%

The individual analyses for this study are presented in the tables and bar graphs appended to this report. All co-operating laboratories are urged to study their performance against the expected accuracy for the various tests and to communicate with us regarding any questions they may have as to the procedures and techniques involved.

DISCUSSION OF RESULTS

Statistical comparisons in this report were developed from the deviations from known quantities added to the sample. The range of deviations considered acceptable to the program were based on the precision and accuracy values as presented in "Standard Methods" for the various tests involved. Table I, below, is a summary of the expected accuracy for the various tests from "Standard Methods" and the ranges acceptable to the Water Quality Network for this reference sample.

TABLE I

ACCEPTABLE LIMITS OF ACCURACY

	Standard Methods	Water Quality Program
Dissolved Oxygen	± 0.1 mg/l	± 0.2 mg/l
Biochemical Oxygen Demand	± 0.11 mg/l	± 0.33 mg/l
Chemical Oxygen Demand	± 1.6 mg/l	± 3.2 mg/l
Ammonia Nitrogen (direct Nessler)	± 0.1 mg/l	± 0.1 mg/l

The Tenth Edition of "Standard Methods" gives the expected precision and accuracy for each test, within the range of concentration normally encountered in water analysis. These "standards of accuracy" should be attainable by most laboratories performing these routine examinations. The additional errors, allowable for the Network Program, are intended only as a guide to the cooperating laboratories and are not to be considered as the ultimate goal in the achievement of laboratory accuracy. The principal reason for the additional allowance is that each determination in this study involved a double analysis, one on raw water and one on river water plus sample, thus compounding the possible error. The B.O.D. and C.O.D. error allowance are the same as for the first study but the "correct" result has been expanded as discussed on Page 2.

DISSOLVED OXYGEN - 2.12 mg/l

Because the preparation of a stable reference sample containing a known quantity of dissolved oxygen is impractical, this test was evaluated by using a reagent which would produce a calculated reduction in dissolved oxygen when added to a duplicate sample. The analyst collected duplicate samples of river water by the proper D.O. sampling technique. He then determined the D.O. on one of the samples and repeated the analysis after adding a prescribed quantity of reference solution A to the second bottle. The decrease in D.O., if the test was performed properly, should be 2.12 mg/l ± 0.2.

Of the 36 laboratories reporting this analysis, 26 submitted results within acceptable limits. Possible reasons for the gross errors reported by several laboratories may be improper sampling, inaccurate pipetting of the reference sample into the D.O. bottle, too much delay between determinations permitting the second portion of water to warm up, thereby reducing the dissolved oxygen level, and improperly standardized reagents.

BIOCHEMICAL OXYGEN DEMAND - 2.5 - 2.8 mg/l

In this test the analyst collected a large sample of river water and divided it into two parts. Two or more bottles were filled, using the prescribed technique; one of these was analysed for initial D.O. and the remainder incubated for 5 days. To the second portion of the large sample was added a specified volume of Solution B. Two or more bottles were filled as before; one of these was analysed for initial D.O., and the remainder incubated concurrently with the first series. After the 5 day D.O. was determined for the incubated samples, the B.O.D. for each series was calculated. The series containing the reference sample should have resulted in an increased B.O.D. of 2.5 to 2.8 mg/l.

Thirty-four laboratories reported this determination and only 15 came within the acceptable limits of accuracy. Of the 19 groups which did not obtain acceptable results, 17 were below the acceptable limit and only 2 were above it. This non-random distribution of failures is indicative of the difficulty of attaining complete oxidation of an organic material if all standard conditions are not properly adhered to. Indeed, it was anticipated that laboratories No. 9, 10, 12, and 13 would obtain low results because of reasons previously stated, either scarcity of micro-biological forms or lack of nutrient elements. it is also possible that other groups obtained unsatisfactory results for similar reasons and not because of manipulative failures. It is preferable, however, that every group should consider the possibility of procedural lapses before other causes for failure are accepted.

CHEMICAL OXYGEN DEMAND - 25.2 - 26.6 mg/l

For this measurement the analyst performed the chemical oxygen demand determination on a sample of raw water and on a duplicate to which had been added a specified volume of Solution B. The C.O.D. was calculated for the two determinations and the increase in C.O.D. of the second determination recorded. If the

procedure was carried out properly the increase should have been between 25.2 and 26.6 mg/l of C.O.D. Of the 25 laboratories which performed the measurement, 21 obtained acceptable results, which is a very definite improvement over the previous study.

It should be noted, however, that scrupulous attention to cleanliness of glassware and standarization of the reagents must be followed for good results on this determination.

AMMONIA NITROGEN - 0.30 mg/l

This test is similar to others in that the raw sample is analyzed for ammonia both before and after the addition of Solution C, a standard ammonia solution. The difference between the two readings should have been 0.30 mg/l $\pm$ 0.1. The results of this determination were good, with 20 of the 31 reporting groups obtaining acceptable results.

Reasons for failure include weak Nessler reagent, incorrect standards and arithmetic errors, each of which may contribute to low results. Contamination from ammonia fumes in the laboratory and especially on laboratory glassware or in dilution water may contribute to high results.

Laboratory 22 reported a leak in an ammonia feeder which caused high results when the sample was examined.

REASONS FOR FAILURE TO OBTAIN ACCURATE RESULTS

C. O. D.

High Results

1. Normality of dichromate solution too low.
2. Normality of ferrous ammonium sulfate too high.
3. Extraneous organic material present - i.e. greasy glassware.
4. Too much of Solution B added.

Low Results

1. Normality of dichromate solution too high.
2. Normality of ferrous ammonium sulfate too low.
3. Insufficient reflux time.
4. Insufficient H_2SO_4 - i.e. less than 50% total volume in flask.
5. Sample too warm when titrated with ferrous ammonium sulfate. (destruction of indicator)
6. Not enough of Solution B added.

REASONS FOR FAILURE TO OBTAIN ACCURATE RESULTS

B. O. D.

High Results

1. Initial D.O. measurement too low.
2. Incubation of 5-day sample at temperature above 20°C.
3. Improper sampling.
4. Too much of Solution B added.
5. Failure to deaerate cold sample - i.e. when O_2 content is above saturation.

Low Results

1. Initial D.O. measurement too high.
2. Lack of seed organisms.
3. Lack of nutrient elements in raw water, i.e. nitrogrn and phosphorus.
4. Improper sampling.
5. Incubation of 5-day sample at temperature below 20°C.

REASONS FOR FAILURE TO OBTAIN ACCURATE RESULTS

Dissolved Oxygen

High Results

1. Too much of Solution A added.
2. Normality of standard thiosulfate low.
3. Faint end point due to deteriorated starch solution.
4. Interference from nitrites-i.e. omission of sodium azide from alkaline iodide solution.
5. Exposure to air after alkaline iodide addition.

Low Results

1. Too little of Solution A added.
2. Normality of standard thiosulfate high.
3. Warming of sample before reagent addition.
4. Failure to mix sample completely after addition of alkaline iodide.

REASONS FOR FAILURE TO OBTAIN ACCURATE RESULTS

Ammonia Nitrogen

High Results

1. Too much of Solution C added.
2. Contamination by extraneous ammonia, i.e. ammonia in distilled water, laboratory fumes, etc.
3. Incorrect standards.

Low Results

1. Too little of Solution C added.
2. Incorrect standards.
3. Weak Nessler reagent.

TABLE I - DISSOLVED OXYGEN

2.12 mg/l

Lab. No.	River Water D.O. mg/l	River Water & Solution A mg/l	Difference Due to Solution A mg/l	Deviation mg/l
31	10.40	9.80	0.60	- 1.52
20	12.53	11.13	1.40	- 0.72
12	13.50	12.02	1.48	- 0.64
28	11.67	10.07	1.60	- 0.52
29	9.87	8.17	1.70	- 0.42
35	5.83	4.03	1.80	- 0.32
30	10.27	8.40	1.87	- 0.25
6	8.26	6.33	1.93	- 0.19
13	13.47	11.50	1.97	- 0.15
4	12.60	10.60	2.00	- 0.12
5	12.30	10.30	2.00	- 0.12
19	12.20	10.20	2.00	- 0.12
33	10.93	8.93	2.00	- 0.12
37	11.40	9.40	2.00	- 0.12
25	8.39	6.38	2.01	- 0.11
7	7.72	5.70	2.02	- 0.10
36	8.93	6.90	2.03	- 0.09
27	12.87	10.80	2.07	- 0.05
10	8.80	6.72	2.08	- 0.04
3	8.95	6.83	2.12	0.00
17	8.75	6.65	2.15	+ 0.03
2	10.02	7.87	2.15	+ 0.03
21	11.30	9.15	2.15	+ 0.03
18	11.64	9.48	2.16	+ 0.04
32	10.54	8.36	2.18	+ 0.06
38	9.60	7.42	2.18	+ 0.06
9	13.50	11.30	2.20	+ 0.08
15	12.55	10.35	2.20	+ 0.08
14	11.17	8.96	2.21	+ 0.09
11	12.57	10.35	2.23	+ 0.11
39	11.55	9.30	2.25	+ 0.13
8	12.63	10.36	2.27	+ 0.15
16	13.77	11.47	2.30	+ 0.18
24	12.15	9.65	2.50	+ 0.38
23	12.63	10.05	2.58	+ 0.46
34	13.09	10.37	2.72	+ 0.60
Avg.	11.06	9.04	2.02	0.23

TABLE II - B.O.D.

2.5-2.8 mg/l

Lab. No.	River Water B.O.D mg/l	River Water & Sample B - B.O.D. mg/l	Diff. Due to Sample B-B.O.D. mg/l	Deviation mg/l
28	0.7	1.2	0.5	- 2.0
31	1.4	2.7	0.9	- 1.6
30	1.3	2.7	1.4	- 1.1
2	1.3	2.7	1.4	- 1.1
9	0.4	2.0	1.6	- 0.9
23	0.7	2.3	1.6	- 0.9
24	3.8	5.4	1.6	- 0.9
35	0.8	1.6	1.6	- 0.9
11	2.7	4.4	1.7	- 0.8
12	1.2	3.0	1.8	- 0.7
27	1.8	3.7	1.9	- 0.6
36	1.6	3.5	1.9	- 0.6
13	0.8	2.8	2.0	- 0.5
29	1.3	3.3	2.0	- 0.5
37	1.1	3.1	2.0	- 0.5
25	2.4	4.5	2.1	- 0.4
10	1.0	3.1	2.1	- 0.4
18	2.5	4.8	2.3	- 0.2
6	1.3	3.7	2.4	- 0.1
15	3.4	5.8	2.4	- 0.1
5	2.0	4.5	2.5	0.0
34	0.3	2.8	2.5	0.0
3	0.5	3.1	2.6	0.0
7	1.6	4.2	2.6	0.0
21	1.5	4.1	2.6	0.0
14	1.7	4.3	2.6	0.0
17	1.9	4.7	2.8	0.0
38	0.9	3.7	2.8	0.0
16	1.7	4.6	2.9	+ 0.1
4	1.4	4.4	3.0	+ 0.2
39	0.6	3.8	3.2	+ 0.4
8	2.8	6.8	4.0	+ 1.2
Avg.	1.51	3.63	2.16	0.52

TABLE III - C.O.D.

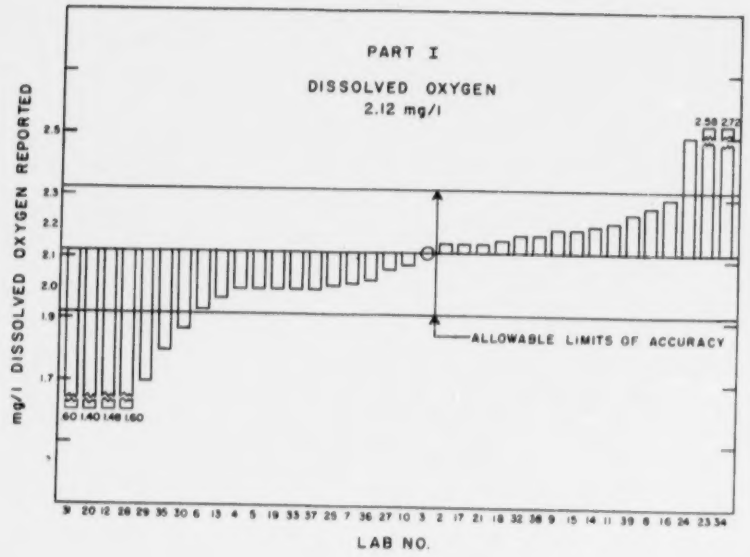
25.2 - 26.6 mg/l

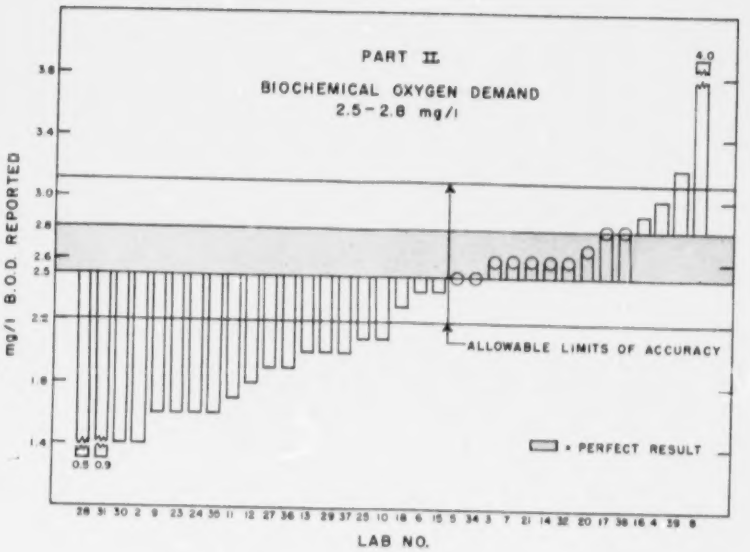
Lab. No.	River Water C.O.D. mg/l	River Water & Sample B - C.O.D. mg/l	Diff. Due to Sample B, COD mg/l	Deviation mg/l
37	31.0	35.0	4.0	- 21.2
39	38.8	54.8	16.0	- 9.2
11	32.0	54.0	22.0	- 3.2
34	5.8	28.4	22.6	- 2.6
27	13.2	36.1	22.9	- 2.3
8	5.3	28.5	23.3	- 1.9
10	66.6	90.1	23.5	- 1.7
18	19.4	42.9	23.5	- 1.7
23	7.2	30.8	23.6	- 1.6
29	21.0	45.0	24.0	- 1.2
7	19.5	43.6	24.1	- 1.1
36	9.3	33.7	24.4	- 0.8
6	21.5	46.2	24.7	- 0.5
17	18.8	43.6	24.8	- 0.4
4	6.0	31.0	25.0	- 0.2
13	10.4	36.1	25.7	0.0
9	3.0	29.2	26.2	0.0
38	15.8	42.5	26.7	+ 0.1
32	6.7	33.6	26.9	+ 0.3
25	21.3	48.2	26.9	+ 0.3
21	27.2	54.7	27.5	+ 0.9
1	13.1	41.8	28.7	+ 2.1
12	4.7	34.0	29.3	+ 2.7
31	7.8	42.7	34.9	+ 8.3
5	6.5	45.0	38.5	+ 11.9
Avg.	17.27	42.06	24.79	3.05

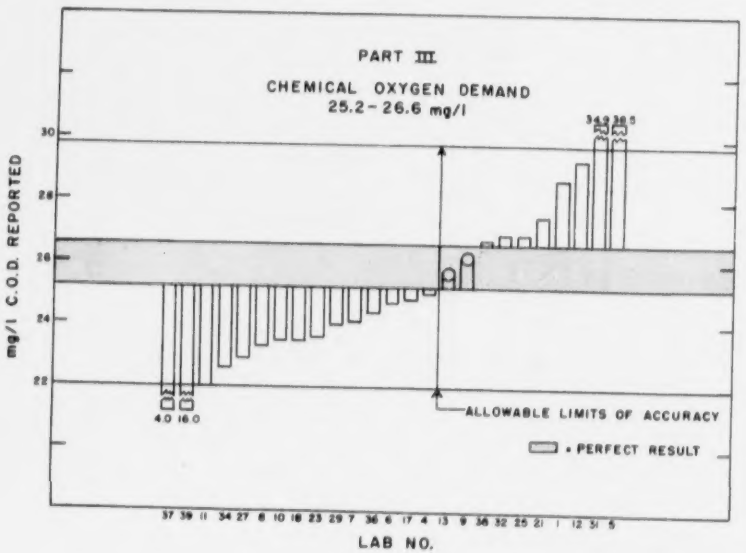
TABLE IV - AMMONIA

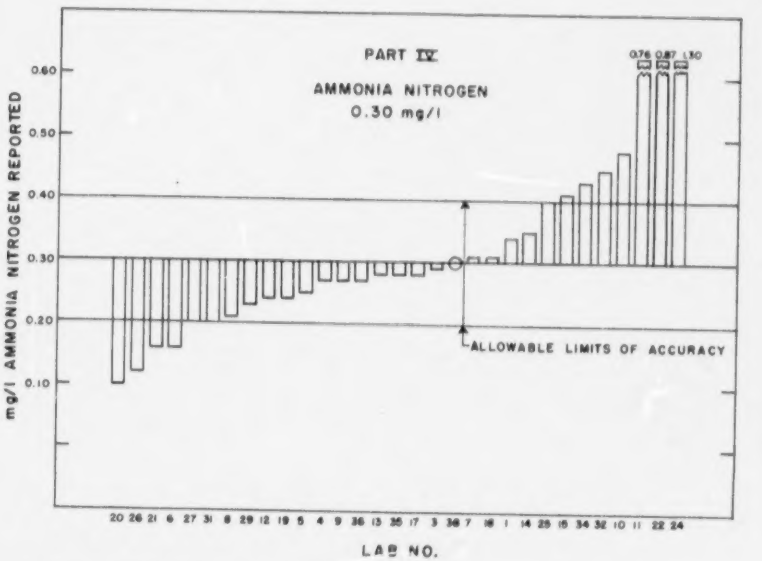
0.30 mg/l

Lab. No.	River Water NH_3-N mg/l	River Water and Solution C NH_3-N mg/l	Diff. Due to Sample C, NH_3-N mg/l	Deviation mg/l
20	0.10	0.25	0.10	- 0.20
26	0.33	0.45	0.12	- 0.18
21	0.14	0.30	0.16	- 0.14
6	0.21	0.37	0.16	- 0.14
27	0.06	0.26	0.20	- 0.10
31	0.08	0.28	0.20	- 0.10
8	0.26	0.47	0.21	- 0.09
29	0.13	0.36	0.23	- 0.07
12	0.01	0.25	0.24	- 0.06
19	0.04	0.28	0.24	- 0.06
5	0.07	0.32	0.25	- 0.05
4	0.16	0.43	0.27	- 0.03
9	0.01	0.28	0.27	- 0.03
36	0.06	0.33	0.27	- 0.03
13	0.06	0.34	0.28	- 0.02
35	0.44	0.72	0.28	- 0.02
17	0.43	0.71	0.28	- 0.02
3	0.56	0.85	0.29	- 0.02
38	0.09	0.39	0.30	0.00
7	0.04	0.35	0.31	+ 0.01
18	0.35	0.66	0.31	+ 0.01
1	0.12	0.46	0.34	+ 0.04
14	0.29	0.64	0.35	+ 0.05
25	0.28	0.68	0.40	+ 0.10
15	0.79	1.20	0.41	+ 0.11
34	0.12	0.55	0.43	+ 0.13
32	0.01	0.46	0.45	+ 0.15
10	0.17	0.65	0.48	+ 0.18
11	0.03	0.79	0.76	+ 0.46
22	0.20	1.07	0.87	+ 0.57
24	0.30	1.60	1.30	+ 1.00
Avg.	0.19	0.54	0.35	0.13









ANALYTICAL REFERENCE SAMPLE TYPE II BD-2

15.